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Reduction of Dithiocarbonates as a Novel Route to Dithiolene Compounds of Uranium. Crystal Structure of the First Bimetallic Dithiolene Complex of an f-Element

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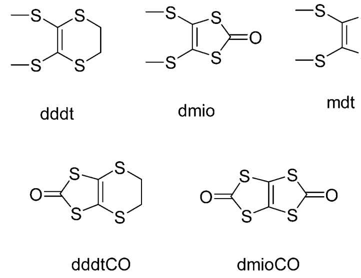
Summary: Reaction of $[U(COT)(BH_4)_2(THF)]$ (COT = η-C_8H_8) with the dithiocarbonates dddtCO and dmioCO (dddt = 5,6-dihydro-1,4-dithiine-2,3-dithiolate; dmio = 1,3-dithiole-2-one-4,5-dithiolate) gave the neutral dithiolene compounds $[U(COT)(dithiolene)]_2$ in good yields (dithiolene = dddt, dmio, or 1,3-dithiole-4,5-dithiolate (mdt)). The X-ray crystal structures of $[U(COT)(mdt)]_2$ and $[U(COT)(mdt)(pyridine)_2]$ show the interaction between the C═C double bond of the mdt ligand and the uranium atom, and the ^1H NMR spectra reveal the facile dithiolene ring inversion process in solution.

Introduction

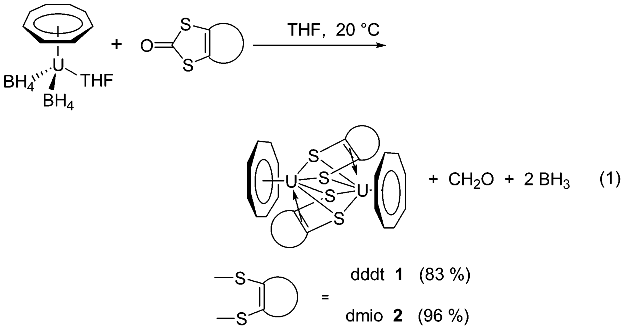
The fascinating variety of structures and physicochemical properties of metal dithiolene complexes led us to introduce the f-elements in these types of compounds. First examples of such crystallographically characterized derivatives were prepared by treatment of uranium chlorides or borohydrides with the sodium salt of the dithiolene anion $dddt^{2-}$ (dddt = 5,6-dihydro-1,4-dithiine-2,3-dithiolate).[1] However, this classical synthesis proved to be tricky in many cases, because of the tedious elimination of salts and the ready formation of anionic addition complexes in place of simple metathesis products. To avoid these difficulties, which are pervasive in the chemistry of the lanthanides and actinides, we have devised an alternative efficient route to the neutral uranium dithiolene compounds. This novel method was inspired by the reductive fission of cyclic dithiocarbonates,[2] considering that the reduction could be achieved by a uranium borohydride. Here we report on the application of this new strategy to the synthesis of the dimeric complexes $[U(COT)(dithiolene)]_2$ (COT = η-C_8H_8) with the bridging dithiolene ligands dddt, dmio, and mdt, which are represented in Scheme 1 (dmio = 1,3-dithiole-2-one-4,5-dithiolate, mdt = 1,3-dithiole-4,5-dithiolate); we also present the X-ray crystal structures of $[U(COT)(mdt)]_2$ and its pyridine adduct $[U(COT)(mdt)(pyridine)_2]$, which show the interaction between the C═C double bond of the mdt group and the metal center, and describe the ^1H NMR spectra, which reveal the facile ring inversion process of the dithiolene ligand.

Scheme 1



Results and Discussion

Synthesis of the Complexes. The synthesis of the neutral uranium dithiolene compounds $[U(COT)(dithiolene)]_2$ (dithiolene = dddt (**1**) and dmio (**2**)), depicted by eq 1, consists of the reduction of dddtCO and dmioCO, the protected forms of the corresponding dithiolene ligands (Scheme 1), by $[U(COT)(BH_4)_2(THF)]$;[3] formation of methanol, resulting from the reaction of formaldehyde and borane, is also observed. Thus, treatment of the uranium bisborohydride with dddtCO in THF gave a dark solution, which, upon standing for 12 h at 20 °C, deposited dark green needles of **1**; the concomitant formation of methanol and $BH_3{\cdot}THF$ was confirmed by NMR and GLC analyses. After filtration and drying under vacuum, the product was isolated in 83% yield. By comparison, transmetalation of $[U(COT)(BH_4)_2(THF)]$ and 1 equiv of Na_2dddt gave a mixture of **1** and the anionic compound $[Na(THF)_x]_2[U(COT)$-



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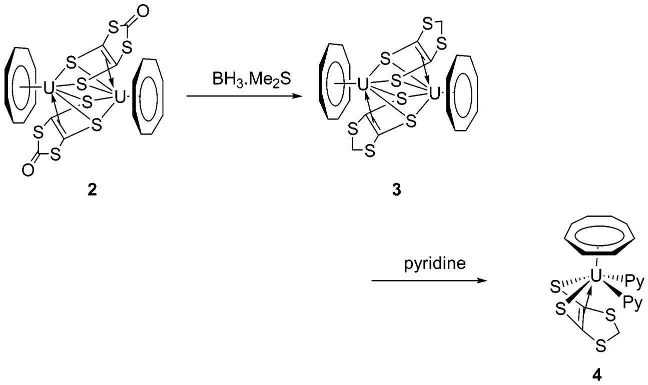
Scheme 2



(dddt)$_2$]; the latter was the sole uranium product after further addition of Na$_2$dddt.[1] Black crystals of the dmio compound **2** were similarly obtained in 96% yield by reduction of dmioCO with [U(COT)(BH$_4$)$_2$(THF)] at room temperature. However, **2** was slowly transformed into the mdt derivative **3**, and when the reaction mixture was heated under reflux, black crystals of **3** were formed after 4 days with a 65% yield. Complex **3** was also obtained by treating **2** with BH$_3$·Me$_2$S in THF (Scheme 2); after 4 days at 65 °C, the mixture was evaporated to dryness to give **3** in almost quantitative yield (NMR experiment). The conversion of **2** into **3** is similar to that of [Ti(Cp)$_2$(dmit)] (Cp = η-C$_5$H$_5$, dmit = 1,3-dithiole-2-thione-4,5-dithiolate) into [Ti(Cp)$_2$(mdt)] by means of borane.[4]

Complexes **1** and **2** have been characterized by their elemental analyses (C, H, S), and **3** has been characterized by its X-ray crystal structure. The ^{1}H NMR spectra of these dimeric compounds could not be recorded because of their insolubility in noncoordinating solvents; in pyridine, the complexes were transformed into the mononuclear Lewis base adducts (vide infra).

Crystal Structures of [U(COT)(mdt)]$_2$ and [U(COT)(mdt)(pyridine)$_2$]. The insolubility of complexes **1**−**3** in poorly coordinating solvents (THF and toluene) and the steric and electronic unsaturation of the U(COT)(dithiolene) moiety suggested that the compounds exist as dimers in the solid state. This was confirmed by the X-ray crystal structure of **3**, which is shown in Figure 1 together with selected data. The two U(COT) units are linked by the four bridging sulfur atoms of the dithiolene ligands; the middle of the U−U′ segment is an inversion center. The structure of **3** can be compared with that of the bisthiolate compound [U(COT)(SPr^i)$_2$]$_2$[5] and those of the various d transition metal complexes of general formula [M(Cp)(dithiolene)]$_2$, like [V(Cp)(S$_2$C$_6$H$_4$)]$_2$[6] and [Mo(Cp)(S$_2$C$_2$H$_2$)]$_2$.[7] In these centrosymmetric molecules, the four bridging S atoms or the two S$_2$C$_2$ fragments of the dithiolene ligands are in the plane that bisects the M−M vector; this plane is parallel to the planar COT or Cp rings. Quite different features are observed in **3**: (a) the U−S1 and U−S2 bond lengths of 2.810(2) and 2.816(2) Å are significantly shorter, by 0.13 Å, than the U−S1′ and U−S2′ distances, and the dihedral angle between the S1S2S1′S2′ plane and the bisecting plane of the U−U′ segment is 4°; (b) this bisecting plane intersects the two COT rings with a dihedral angle of 12°; and (c) most notably, the S$_2$C$_2$S$_2$ fragment of the mdt ligand is far outside the bisecting plane of the U−U′ segment, forming a dihedral angle of 60°. This deviation, which corresponds to an important folding of 81.9(2)° of the US1S2C1C2 ring along the S1−S2 axis, brings the C1 and C2 atoms in close contact with the uranium atom. The U−C1 and U−C2 bond lengths of 2.950(8) and 2.948(8) Å are similar to the average U−C distances in the uranium(IV) arene complexes [{UCl$_2$(η-C$_6$Me$_6$)}$_2$(μ-Cl)$_3$][AlCl$_4$] (2.92(4) Å) and [{UCl$_2$(η-C$_6$Me$_6$)}$_2$UCl$_5$] (2.94(3) Å).[8] This interaction between the C=C double bond of the dithiolene ligand and the metal center, which is unprecedented in bimetallic dithiolene compounds, is clearly responsible for the distortion of the U$_2$S$_4$C$_4$ fragment from D_{2h} symmetry.

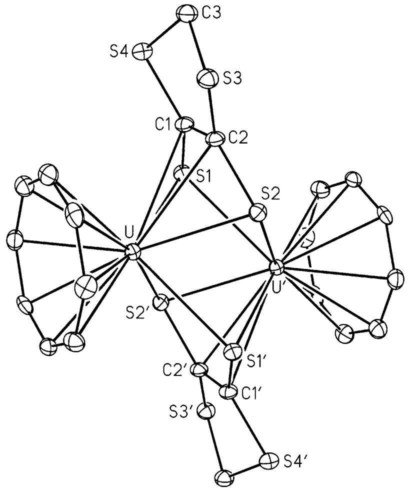


Figure 1. View of complex **3**. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Symmetry code: ′ = −x, 1−y, −z. Selected bond distances (Å) and angles (deg): U−S1 2.810(2), U−S2 2.816(2), U−S1′ 2.946(2), U−S2′ 2.945(2), U−C1 2.950(8), U−C2 2.948(8), ⟨U−C(COT)⟩ 2.64(2), C1−C2 1.37(1),C1−S1 1.747(8), C1−S4 1.770(8), C2−S2 1.747(8), C2−S3 1.767(8), U···U′ 3.633(1); S1−U−S2 71.98(6), S1′−U−S2′ 68.29(6), C1−U−C2 26.8(2).

The dissolution of complexes **1**−**3** in pyridine is related to the cleavage of their dimeric structure and formation of mononuclear Lewis base adducts. A solution obtained from **3** deposited brown crystals of [U(COT)-(mdt)(pyridine)$_2$] (**4**) (Scheme 2), the structure of which is represented in Figure 2. The U−N1 and U−N2 distances of 2.69(1) and 2.636(9) Å can be compared with that of 2.64(1) Å in [U(COT)Cl$_2$(pyridine)$_2$].[9] The most interesting feature of the structure is the η^4-coordination of the mdt ligand. The U−S1 and U−S2 distances, which are equal to 2.720(3) and 2.751(3) Å, are ca. 0.08 Å shorter than in **3**; this difference between metal−sulfur bond lengths of bridging and terminal dithiolene ligands was not unexpected. However, it is noteworthy

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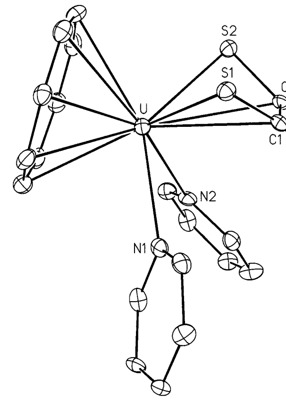


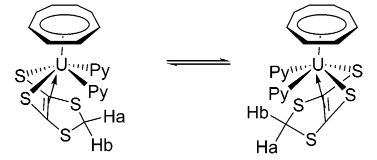
Figure 2. View of complex **4**. Displacement ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): U−S1 2.720(3), U−S2 2.751(3), U−C1 2.89(1), U−C2 2.97(1), U−N1 2.69(1), U−N2 2.636(9), ⟨U−C(COT)⟩ 2.70(3), C1−C2 1.39(2), C1−S1 1.73(1), C1−S4 1.78(1), C2−S2 1.75(1), C2−S3 1.75(1); S1−U−S2 77.1(1), C1−U−C2 27.4(3), N1−U−N2 74.3(3).

that the interaction between the C1−C2 bond and the metal center has been preserved upon addition of pyridine and seems as strong as in **3**, in view of the U−C1 and U−C2 distances of 2.89(1) and 2.97(1) Å. The folding dihedral angle of the mdt group [75.6(3)°] is also similar to that measured in **3**, but the dithiolene ligand adopts here an *endo* conformation around the metal atom.

In both compounds **3** and **4**, the characteristics of the mdt ligand, i.e., the $C(sp^2)$−S distances [average 1.76(2) Å in **3** and 1.75(3) Å in **4**] and C═C distances [1.37(1) Å in **3** and 1.39(2) Å in **4**], are consistent with those found in $[NBu_4][Ni(mdt)_2]$ [1.74(2) and 1.36(2) Å].[10] Although the folding dihedral angles in **3** and **4** are far more important than those encountered in the titanium dithiolene complexes $[Ti(Cp)(dmit)_2]^-$ (22.00(5)° and 62.53(3)°)[4] and $[Ti(Cp)(S_2C_6H_4)_2]^-$ (36.3° and 23.3°)[11] or the enedithiolate derivative $[Ti(Cp)_2(S_2C_2H_4)]$ (46.1°),[12] suggesting a greater stabilization of the σ^2,π-structure, the ethylenic C1−C2 bonds are not elongated any more by interaction with the uranium center. The structural features of the dithiolene ligands in **3** and **4** are reminiscent of those of group 4[13] and thorium[14] diene complexes in which a susbstantial amount of σ^2,π-metallacyclopentene character is present. The C_8H_8 rings are planar within ±0.03 Å, and the uranium−carbon distances, which average 2.64(2) Å in **3** and 2.70(3) Å in **4**, are within the range of U−C(COT) bond lengths, which vary from 2.62(2) Å in $[U(COT)(SPr^i)_2]_2$[5] to 2.71(4) Å in $[U(COT)(NEt_2)(THF)_3][BPh_4]$.[15]

Dynamic Behavior of the Compounds in Solution. The mononuclear complexes [U(COT)(dddt)(pyridine)$_2$] and [U(COT)(mdt)(pyridine)$_2$], formed by dissolution of **1** and **3** in pyridine-d_5, exhibit fluxional behavior in solution, as shown by variable-temperature ^{1}H NMR experiments. At 80 °C, the dithiolene groups give rise to a single signal, the four protons of the dddt ligand and the two protons of the mdt ligand being magnetically equivalent. By lowering the temperature, these resonances are broadened, and coalescence is observed at −30 °C and +30 °C for the dddt and mdt compounds, respectively. Two signals of equal intensities (2 H), corresponding to the dithiolene ligand, are visible on the spectrum of the dddt derivative at −40 °C; only one peak (1 H) is detected for the mdt analogue at low temperature, the other one being masked by the solvent resonances. The dynamic behavior of the complexes, revealed by the interchange of the magnetically nonequivalent methylene protons of the dddt and mdt ligands, can be ascribed to the rapid ring inversion represented in Scheme 3. From line shape analysis of the spectra, the free energies of activation for this process are 10.2(3) and 12.0(3) kcal mol^{-1} for the dddt and mdt ligands, at −40 and −30 °C, respectively. The lower barrier in the dddt derivative would reflect the greater steric interaction between the dithiolene and pyridine ligands in the ground state of the complex. These $\Delta G^\ddagger$ values are in the range of those calculated for the metallacyclopropene ring inversion in bis(cyclopentadienyl)diene compounds of group 4 metals and actinides.[14]

Scheme 3



Conclusion

The reactions of [U(COT)(BH$_4$)$_2$(THF)] with the dithiocarbonates dddtCO and dmioCO represent a novel route to neutral dithiolene complexes of uranium. This extremely simple synthesis is more efficient and seems a much more attractive concept to us than the classical salt exchange reaction. The crystal structures of **3** and **4** and the fluxional behavior of the complexes in solution reveal the significant interaction between the C═C double bond and the uranium center.

Experimental Section

All reactions were carried out under argon (<5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a glovebox. Solvents were dried by standard methods and distilled immediately before use. The ^{1}H NMR spectra were recorded on a Bruker DPX 200 instrument and referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany). [U(COT)(BH$_4$)$_2$(THF)],[3] dddtCO,[16] and dmioCO[17] were prepared by published methods.

[U(COT)(dddt)]$_2$, 1. A flask was charged with [U(COT)(BH$_4$)$_2$(THF)] (400 mg, 0.901 mmol) and dddtCO (300 mg, 1.44 mmol), and THF (50 mL) was condensed in. The reaction mix-

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ture was allowed to stand for 12 h at 20 °C, without stirring, and dark green needles of **1** were deposited. The crystals were filtered off, washed with THF (2 × 20 mL), and dried under vacuum (392 mg, 83%). Anal. Calcd for $C_{24}H_{24}S_8U_2$: C, 27.58; H, 2.31; S, 24.55. Found: C, 27.49; H, 2.16; S, 24.42.

[U(COT)(dmio)]$_2$, 2. A flask was charged with [U(COT)-$(BH_4)_2$(THF)] (82 mg, 0.18 mmol) and dmioCO (57.7 mg, 0.28 mmol), and THF (25 mL) was condensed in. The reaction mixture was allowed to stand for 30 min at room temperature, without stirring, and black crystals of **2** were deposited. The crystals were filtered off, washed with THF (2 × 20 mL), and dried under vacuum (105 mg, 96%). Anal. Calcd for $C_{22}H_{16}O_2S_8U_2$.2(THF): C, 30.30; H, 2.71; S, 21.57. Found: C, 30.17; H, 2.84; S, 21.36.

[U(COT)(mdt)]$_2$, 3. (a) A flask was charged with [U(COT)-$(BH_4)_2$(THF)] (309 mg, 0.69 mmol) and dmioCO (145 mg, 0.69 mmol), and THF (25 mL) was condensed in. The reaction mixture was heated at 80 °C for 4 days, without stirring, and black crystals of **3** were deposited. The crystals were filtered off, washed with THF (2 × 20 mL), and dried under vacuum (237 mg, 65%).

(b) An NMR tube was charged with **2** (9.5 mg, 0.18 mmol) and THF-d_5 (0.4 mL). $BH_3 \cdot Me_2S$ (18 mL of a 2 M Et_2O solution) was added via a syringe. After 4 days at 65 °C, the mixture was evaporated to dryness to give **3** in almost quantitative yield.

[U(COT)(mdt)(pyr)$_2$], 4. Complex **3** (100 mg) was dissolved in pyridine (25 mL). The solution was evaporated to dryness, leaving a brown powder of **4**. Anal. Calcd for $C_{21}H_{20}N_2S_4U$: C, 37.83; H, 3.02; S, 19.24. Found: C, 37.60; H, 3.22; S, 19.09. An NMR tube was charged with **4** (ca. 5 mg) in pyridine-d_5 (0.4 mL); on standing at room temperature, the solution deposited brown crystals suitable for X-ray diffraction analysis.

Crystallographic Data. For compound **3**: $C_{22}H_{20}S_8U_2$, M = 1016.92, orthorhombic, space group $Pbca$, a = 16.2897(7) Å, b = 8.7357(3) Å, c = 17.2834(7) Å, V = 2459.46(17) Å^3, Z = 4, D_c = 2.746 g cm^{-3}, μ = 13.844 mm^{-1}, $F(000)$ = 1856. R_1 = 0.032, wR_2 = 0.070, S = 1.031 for 2325 independent reflections (R_{int} = 0.057) and 145 parameters. For compound **4**: $C_{21}H_{20}N_2S_4U$, M = 666.66, monoclinic, space group $P2_1/c$, a = 8.5153(11) Å, b = 16.1129(15) Å, c = 15.763(2) Å, β = 100.568(5)°, V = 2126.1(4) Å^3, Z = 4, D_c = 2.083 g cm^{-3}, μ = 8.038 mm^{-1}, $F(000)$ = 1264. R_1 = 0.055, wR_2 = 0.113, S = 1.006 for 4020 independent reflections (R_{int} = 0.066) and 253 parameters. Data for both compounds were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer[18] using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and processed with DENZO-SMN.[19] The structures were solved by direct methods with SHELXS97 and refined by full-matrix least-squares on F^2 with SHELXL97.[20] Absorption effects were empirically corrected with PLATON.[21] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms in both compounds were introduced at calculated positions and were treated as riding atoms, with an isotropic displacement parameter equal to 1.2 times that of the parent atom. The molecular plots were drawn with SHELXTL.[22] CCDC reference numbers: 198989 (**3**) and 198990 (**4**).

^{1}H NMR Spectra of the Complexes [U(COT)(dithiolene)(pyridine)$_x$]. These compounds were formed upon dissolution of **1**−**3** in pyridine-d_5. [U(COT)(dddt)(pyridine)$_x$], at 20 °C: δ 10.87 (s, $w_{1/2}$ 33 Hz, 4 H, dddt), −30.98 (s, $w_{1/2}$ 12 Hz, 8 H, COT); at −40 °C: δ 20.2 and 15.1 (s, $w_{1/2}$ 500 Hz, 2 × 2 H, dddt), −38.75 (s, $w_{1/2}$ 12 Hz, 8 H, COT). Coalescence of the dddt signal occurred at −30 °C. [U(COT)(dmio)(pyridine)$_x$], at 20 °C: δ −32.07 (s, $w_{1/2}$ 12 Hz, 8 H, COT). [U(COT)(mdt)-(pyridine)$_x$], at 90 °C: δ 11.21 (s, $w_{1/2}$ 35 Hz, 2 H, mdt), −24.82 (s, $w_{1/2}$ 3 Hz, 8 H, COT); at −30 °C: δ 17.08 (s, $w_{1/2}$ 45 Hz, 1 H, mdt), −37.51 (s, $w_{1/2}$ 3 Hz, 8 H, COT). Coalescence of the mdt signal occurred at 30 °C.

Supporting Information Available: Tables giving data collection and refinement details, atomic coordinates, thermal parameters, and bond lengths and bond angles of the crystallographically characterized complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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